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RESEARCH ARTICLE

A COMPARATIVE INVESTIGATION ON PETROLEUM DEMULSIFICATION TECHNIQUES (CENTRIFUGE AND GREEN CHEMICALS VERSUS CONVENTIONAL CHEMICALS)

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ABSTRACT

The breaking (demulsification) of 50-50% w/o petroleum emulsions of two oils (A and B) by Green (chemical and centrifuge) methods were studied in comparison to conventional (chemical) method. The green methods consisted of silicon based chemical demulsifiers and high-speed centrifuge operated at 12,000 RPM, while the conventional method consisted of Amine group based demulsifiers. In chemical method, the concentrations were varied (0.5%, 1.5% and 3%), while in centrifuge method, the processing time was varied (10 and 30 minutes). The efficiency of these methods was determined by measuring the amount of water separated from the emulsion after being treated. The maximum separation efficiencies for Silicon demulsifiers were 93 and 88% for oils A and B respectively, and that of Amine group demulsifiers were 72 and 86% for oils A and B respectively, While centrifuge demulsification gave maximum separations of 39 and 24% for oils A and B respectively. Based on these results, Silicon based demulsifiers are very effective and reliable method to treat emulsions for different types of oils with different composition, and have the potential to be used as an alternative method in the demulsification or breaking of water-in-crude oil emulsions.

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INTRODUCTION

Petroleum, which means (rock oil), originated from combination of two Latin words, petrus (rock) and oleum (oil). It is renowned liquid hydrocarbon based mineral that is claimed to be formed from the sedimentation of the prehistoric biomass and organisms that were deposited in the earth's crust at different sites many eons ego. Then converted under the effect of extremely tough anaerobic physical and mechanical conditions to Kerogens then further to Catagenesis which consist mainly of three fluids (oil, gas, and water) (Nwankwor Emeka Henry, 2013). Even though petroleum oil and water are naturally immiscible at least at their natural states, yet so often they do mix in the oil reservoir where water is either indigenous (in new reservoirs) or injected for enhanced oil recovery (EOR) purposes (in older wells). Thus, they attain an intimate and inseparable state known as petroleum emulsions or water-in-oil emulsion (David Aurthur Redford, 1975). Beside oil reservoir, petroleum emulsion also occurs in other locations throughout the oil mining process such as in drilling, production, transportation and processing.

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Thus far, the most contentious locations for the formation of emulsions in oil mining process are Catagenesis reservoirs, Well bores, Surface facilities, transportation systems and refineries (Sawsan A.M. Mohammmed 2014). Natural occurrence of petroleum emulsions are mostly brought about via the indigenous amphiphilic molecules, which consist mainly of Asphaltenes and resins together with some fatty acids as well as inorganic minerals (Mathew Spiecker *et al.*, 2003). Practically, emulsions are usually unwanted in petroleum industries and ultimately water should be removed to upgrade the quality and purity of the petroleum to standard level (Sawsan *et al.*, 2014). Asphaltenes, are defined as the fraction of petroleum oil that is insoluble and hence precipitate out when petroleum is mixed with normal light alkanes (e.g. Hexane, heptane, and octane). The chemical structure of asphaltene, consists of poly-nuclear aromatic sheets surrounded by hydrocarbon tails, forming colloids having molecular weights range of 500-20,000 $gmol^{-1}$, which in turn very rich in functional groups including some acids and bases. In contrast to asphaltenes, resins which share similar chemical composition to asphaltenes are claimed to be very effective dispersant of asphaltene in petroleum, are defined as the petroleum fractions which can dissolve in light alkanes (e.g.

pentane, Hexane, heptanes) but not in propane (Manar El-Sayed Abdel-Raouf, 2012). Asphaltenes are believed to be one of the major indigenous constituent of petroleum that possess amphiphilic behavior (having surfactant-like character) and responsible of stabilizing the emulsions. During petroleum mining and transportation, the massive turbulence in the flow provides the mixing energy that causes the dispersion of water phase, which is indigenous to the oil reservoir in the oil and vice versa. Then the interfacial active components (Asphaltenes, Resins, Naphthenic acids, minerals, clays, etc…) migrate from the balk to the interface between the droplets and continuous phase forming rigid film encapsulating the droplets that prevents the coalescence of the droplets, and form stable emulsion (Ing Harald Aufle, 2002). Although; emulsion formation seemed to be unavoidable in the oil field, yet, at end of the day, water, has to be separated from petroleum to reduce impurities and meet the standard specification of the crude before processing or sending to market (C. Ijogb emeye).

Several methods have been used thus far to break petroleum emulsions. It involves chemicals, thermal, electrical, or combination of some of these processes with respect to emulsion properties. The current research investigates the effect of some green chemical demulsifiers and ultrasonic techniques in breaking petroleum emulsions in comparison to conventional demulsifiers. The main objective of chemical demulsifiers is to neutralize the effect of emulsifying agent and destroy the interfacial barrier between droplets leading to coalescence. Besides that, a good demulsifiers must have the ability to reduce the viscosity of the emulsion and hence improves the pumping ability. Commercial demulsifiers are generally polymeric surfactants such as copolymers of polyoxyethylene or alkylphenol formaldehyde resins or blinds of various surface-active substances (Ing Harald Aufle, 2002).

Principles of centrifugal separation

Centrifugal separation is the process of separating suspended particles by accelerating sedimentation rate via high-speed rotation. There are three main centrifugal separation methods, which applied in most separation processes. Firstly, Differential pelleting in which the separation rate is driven by particle sizes (gradual fractionation, whereby, large particles sediment at the bottom followed by midsized particles, then the small particles at the top). Secondly, Rate zonal centrifugation, wherein particle separation occurs based on differences in their sedimentation coefficient. Thirdly, isopycnic centrifugation, whereby, particles with similar densities separate based on the slight differences in their density (http://www.hitachi-koki.com/himac). Various types of centrifuges used for separation purposes. Some of which are: Microfuge, large capacity preparative centrifuge, high-speed centrifuge and ultracentrifuge, thus, the selection depends on the task or application required (http://ipmbgazette.weebly.com/uploads/1/0/3/0/1030249/minza.pdf)

Mechanism of centrifugal separation

A centrifuge is a rotating device used to split suspended particles and macromolecules: such as cells, sub-cellular components, proteins, and nucleic acid from mixture based on their size, shape, and density.

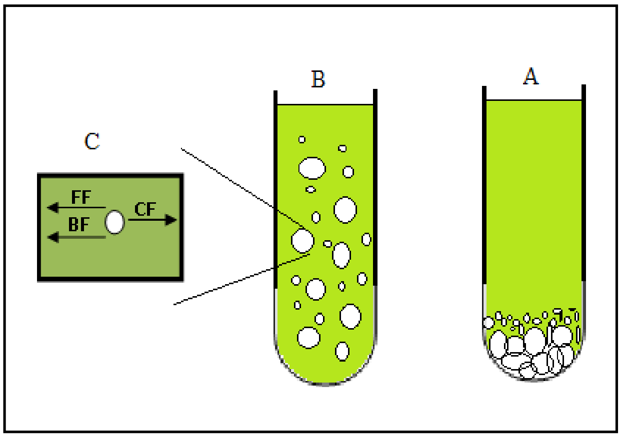

Figure 1: Exaggerated representation of suspended particles exposed to centrifugal force, b) Before centrifugation. a) After centrifugation, c) Forces acting on particles, (CF: Centrifugal forces, FF: Frictional forces, BF Buoyancy force).

Figure1 illustrates roughly the concept of centrifugal separation. Whenever a suspending mixture rotated, the centripetal force induces the particles to break away from the frictional forces and moves away in the radial direction from the axis of rotation. Each suspended particle under centripetal force experiences nearly three essential forces, namely, centrifugal force (CF), frictional resistance against particle moving through suspending fluid or frictional forces (FF), and flotation or buoyancy force (BF). Balancing these three forces yields a net force (F_{Net}) acting on particle under centrifugal forces as given by equation 1 (http://www.phys.sinica.edu.tw/ TIGP- NANO/ Course/2007_ Spring/Class%20Notes/ AC_Chapter%203%20Centrifugation%200321.pdf).

$$F_{Net} = (m_p - m_s)rw^2 - fV \quad \text{………………………………….}(1)$$

Where:

$\boldsymbol{m_p}$, $\boldsymbol{m_s}$ **:** Mass of equal volume of solvent and mass of particle respectively

$\boldsymbol{r}$, : Radius of rotation (centripetal distance of a particle, cm) and mean angular velocity (radians/second) respectively

$\boldsymbol{f}$: Friction coefficient of friction force opposing the movement of particle in the solvent

$\boldsymbol{V}$ **:** Particle velocity

Equation 2 represents the rate of sedimentation of suspended particle in centripetal force.

S = V_t/(w_x^2) = m(1 − V_2 ρ)/f ……………………. (2)

$\boldsymbol{m}$ **:** Mass of suspended particles

$\boldsymbol{f}$ **:** Frictional coefficient of the particles in the solvent

$\boldsymbol{\rho}$ **:** Density of solution

$\boldsymbol{V}$ **:** Particle velocity

Emulsions, whether occurred naturally or manmade artificially, are unwanted in almost every petroleum industry, because of the tremendous troubles they cause to the processing utilities and pipelines.

Emulsified water occupies space in the refinery equipment and storage tanks, as well as alters the physical properties of the crude, mainly density and viscosity. The density of emulsified petroleum oil can increase from 800 $Kg.m^{-3}$ for from pure oil to 1030 $Kg.m^{-3}$ for water/petroleum emulsions, while viscosity could indeed increase from few mPa.s to as high as 1000 mPa.s. Thus far, chemical demulsification is the most commonly used and highly commercialized technique in separating water from petroleum oil. However, most of these chemicals are toxic and harmful to the environment if discharged with separated water, therefore more research still in demand to improve or abate the use of harmful chemical demulsifiers. The objective of this research is to investigate the effect of some green demulsification techniques, mainly Centrifuge and Green chemicals in comparison to the conventional chemicals.

MATERIALS AND METHODS

To accomplish the objective of this study; high-speed centrifuge and two types of chemical demulsifiers were utilized to break the experimentally prepared emulsions. The green chemicals were Silicon based demulsifiers, which were purchased from local company and used as they are, while conventional demulsifiers used in this study, were Hexylamine (amine group demulsifiers)

Samples Preparation and Demulsification Procedures

The crude oil samples were obtained from PETRONAS (Malaysian oil and Gas Company) refinery at Melaka city, two types of crude oils were used for this study denoted as crude oil (A and B), crude oil A from Kuwait oil field and B from Dubai (UAE). Different samples of water-in-oil emulsions were prepared using crude oils A and B, tape water was used as internal phase in all emulsion samples. Span80 was used as emulsifiers. Emulsions were prepared in 500 ml graduated beaker, at fixed water-oil ratios (50-50% w/o). The demulsification experiments were performed using chemical demulsifiers (green versus conventional) and high speed centrifuge as mentioned earlier. Chemical demulsification was performed by first adding the demulsifiers to the experimental newly prepared emulsion sample, then mixed at 500 revolution per minutes (RPM) for 30 seconds, after that the sample (emulsion plus demulsifiers) was poured in a graduated measuring cylinder and left to settle gravitationally. The quantity of water settled at the bottom of the measuring cylinder recorded at different specified intervals. Separation efficiency (e) was calculated using equation 3.

$$e = \frac{voleme\ \ of\ separated\ \ water(ml)}{orginal\ \ volume\ \ of\ \ water\ \ in\ the\ emulsion\ \ (ml)} * 100\% \cdots (3)$$

With regard to centrifugal demulsification, sample was prepared in a centrifugal bottle and processed under highest speed of 12,000 rpm.

RESULTS AND DISCUSSION

The experimented results of this study presented in two parts. Firstly, the effect of chemical demulsification techniques in breaking and separating water from petroleum emulsion investigated. Secondly, centrifugal demulsification technique is studied. In chemical demulsification; the concentration of chemical demulsifiers were varied as such (0.5, 1.5 and 3%), while other parameters such as water/oil ratios (emulsion composition) were kept at 50-50%. In centrifuge demulsification, the rotational speed fixed at 12000 rpm, while the centrifugation time varied (10 and 30 minutes), emulsion composition fixed at (50-50% w/o). Figure 2 shows the separation efficiency for different concentrations of amine group demulsifiers on separating water from petroleum emulsions.

After demulsifiers and emulsions are well mixed, the mixtures then placed in a graduated measuring cylinder and water separation recorded every 24 hours for one week (7 days). The separation efficiency e (%) calculated from equation 3. As shown in figure 2, at 0.5% amine group demulsifires concentration, there was no separation at all with both oils (A and B) through the observation period (one week). However, 1.5% concentration of amine group demulsifiers gave better separation with oil B than oil A and that might be due to the intrinsic properties of the two different crude oils. For oil B, The water separation reached 64% in the first day and remained constant afterward. While for oil A, separation started at day 2 and reached its maximum value of 14% on day 4 and remained constant till day 7. The highest separation efficiency for amine group demulsifiers was observed at their highest concentration (3%) wherein separation efficiency had reached 56% and 76% for oil A and B respectively in the first day, Then reached plateau of 72% for oil A on day 4, and 86% for oil B on day 3 (Figure 2). Based on the current results of amine group based chemical demulsification method, Separation efficiencies were observed to increase proportionally with concentration of demulsifiers, also amine group demulsifiers worked better on oil B than oil A.

Figure 3 represents the effects the various concentrations of the Green demulsifiers (silicon-based demulsifiers) on breaking 50-50% stable water-in-oil (w/o) emulsions of two different types of petroleum (A and B), which prepared just prior to demulsification process. At low concentration of 0.5%, separation efficiencies were 50 and 62 % for oils A and B respectively in the first day, then continued very slowly till reached 70% for A and 63.8% for B on day 7. Similar trend observed at 1.5%, wherein the separation efficiencies were 64% for oil A and 78% for oil B on the first day, then increased gradually to 93% for oil A and 79.4% for oil B on day 7. When the concentrations of silicon based demulsifiers increased to 3%, separation efficiencies reached 72 and 88% with respect to oils A and B in day 1 , then in the subsequent days, the trend increased sharply with oil A and reached 90% on day 7, while it was almost nearly stagnant with oil B which reached 88.4%. The overall observation from this study is that, in Silicon based chemical demulsification technique, the separation efficiencies not necessarily increase gradually with concentration. Thus, The maximum separation efficiencies observed with chemical demulsifiers was 93% and 88.4% for oils A and B respectively, while that of amine group based demulsifiers were 72 and 86% for oils A and B respectively (Figures 2 and 3).

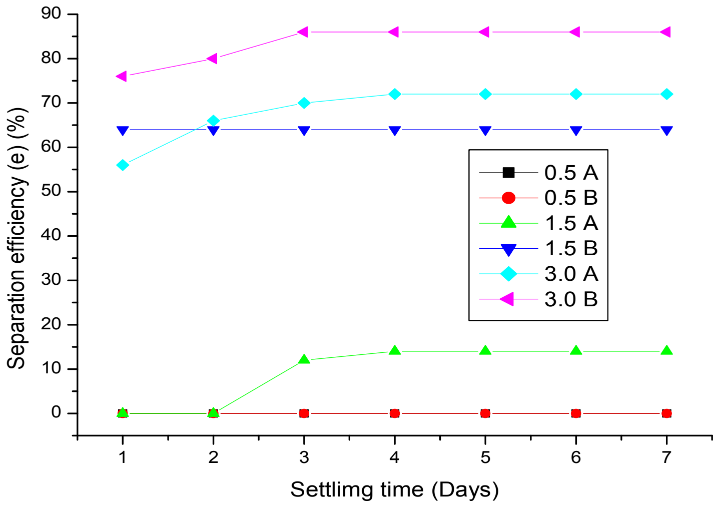

Figure 2. Effects of concentrations of amine group demulsifiers on w/o emulsions of two types of petroleum oils (A and B)

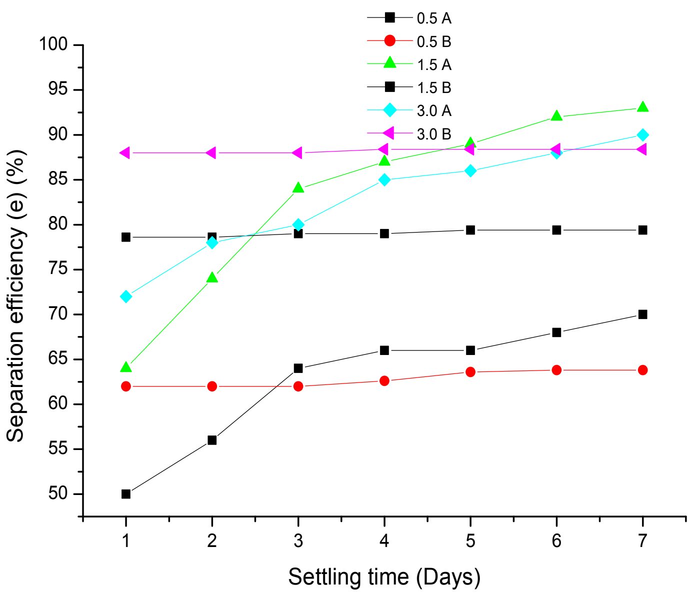

Figure 3. Effect of different concentrations of silicon group demulsifiers on w/o emulsions of two types of petroleum oils (A and B)

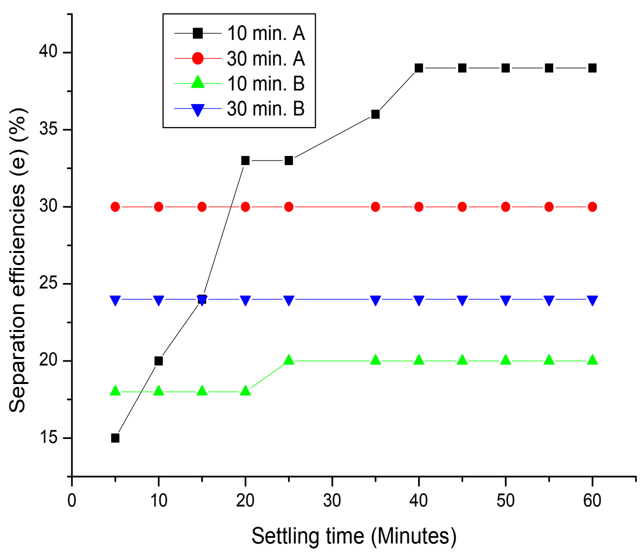

Figure 4. Effect of centrifugation time on w/o emulsions of two types of petroleum emulsions, (centrifuge speed was fixed at 1200 RPM)

Figure 4 represents the effect of high-speed centrifuge on breaking 50-50% water-in-oil emulsions of two different oils at maximum speed of 12,000 RPM, at two different processing times (10 and 30 minutes). Water separation data were collected within settling time of one hour at 5 minutes interval, this is very short compared settling of chemical demulsification method, that is because in centrifugal demulsification, the rate of separations were observed to reach their maximum plateau very soon after sample is placed into measuring cylinder. The maximum separation efficiencies for sample A were 39 and 30% after 10 and 30 minutes operating time respectively. While for oil B the maximum separation efficiencies of 20 and 24% were recorded for processing time of 10 and 30 minutes respectively.

CONCLUSION

A comparative investigation was conducted to assess the effects of some green and environment friendly methods for treating petroleum emulsions of two different crude oils (A and B) in comparison to the conventional chemical demulsifiers. The green chemicals used in this study denoted as Silicon demulsifiers, while the conventional chemicals denoted as Amine group demulsifiers. The maximum separation efficiencies for Silicon demulsifiers were 93 and 88% for oils A and B respectively, and that of Amine group demulsifiers were 72 and 86% for oils A and B respectively, While centrifuge demulsification gave maximum separations of 39 and 24% for oils A and B respectively. Based on this experimental results, it could be concluded that Silicon based demulsifiers are very effective and reliable method to treat emulsions for different types of oils with different composition, and have the potential to be used as an alternative method in the demulsification or breaking of water-in-crude oil emulsions.

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